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X-ray Diffraction Study of Bi-layer and Tri-layer PbSe-SnSe Superlattices

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X-ray diffraction study of a $(PbSe)_n(SnSe)_m$ artificial superlattice grown by the vacuum evaporation method is reported. The subscripts n and m indicate that the structure is a repeating sequence of n monolayers of PbSe followed by m monolayers of SnSe. For samples with (n,m)=(2,2) and (3,3) strong and sharp superlattice reflections were observed, which confirmed that the desired superstructures were constructed coherently along the growth direction even in the samples with such short periods. In addition, it was found from measurements of the rocking curve of the basic reflection that the coherence within the film plane is drastically improved by decreasing n or m.

KEY WORDS: Superlattice/ PbSe-SnSe/ X-ray diffraction/

INTRODUCTION

Modern developments of the vapour phase deposition methods have enabled to synthesize compositionally modulated films called Artificial Superlattice (ASL). Various types of ASL's have been obtained by controlling the thickness of a couple of materials in the atomic scale and depositing them alternately. In particular, there are a lot of work on ASL's composed of lattice-matched materials like GaAs-AlAs, which show that single crystal ASL films can be synthesized for such combinations[1-3]. From the viewpoint of creating new materials and new properties by constructing ASL structure, however, it is more interesting to choose lattice-mismatched materials for the sake of variety in various aspects. It may open a new field of material science to combine in the atomic scale two materials with different crystal structures and different properties. There have been few reports, however, on the synthesis of coherent ASL films made of constituents having a large lattice mismatch over 1% or different symmetries. We have tried to synthesize a coherent ASL composed of PbSe and SnSe[4]; PbSe has the cubic NaCl-type structure, whereas SnSe has the orthorhombic SnS-type structure (a kind of distorted NaCl-type structure). Moreover, the lattice mismatch between them is quite large, about 3%. The samples were designated $(PbSe)_n(SnSe)_m$, implying n (001) atomic planes of PbSe and m (001) atomic planes of SnSe being stacked per modulation wavelength Λ. As a result of structural analysis on the samples with m and n larger than 5 by the use of the x-ray diffraction method and transmission electron microscopy observations of the cross-section of the films, it was found that the compositional modulation could be described by the step model. In addition, we observed a change of crystal symmetry in the PbSe layers: PbSe adopted the SnS-type struc-

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ture when the thickness was less than 30 Å for coherency strain, but it relaxed back to the NaCl-type structure when the thickness was larger. More recently, we have prepared samples with shorter periods, both n and m being less than 5. These samples were expected to be ASL's having the SnS-type structure. In this letter, we report mainly the structural characteristics of $(PbSe)_n(SnSe)_m$ with (n,m)=(2,2) and (3,3) and the change of the crystalline quality depending on m and n.

EXPERIMENTS

Samples with (n,m)=(2,2), (3,3), (8,8) and (30,30) were grown by evaporating the compounds of PbSe and SnSe in a high vacuum ($2\cdot10^{-6}$ torr) onto hot (150°C) sodium chloride which was cleaved in air and subsequently set in the vacuum chamber. The growth rate was less than 1 Å/s. The details of sample preparation have been described in our previous report[4]. The structure of obtained films was examined by the x-ray diffraction (XRD) method. The x-ray measurements were made using Cu-Kα radiation generated from a Rigaku rotating anode x-ray source and a conventional 2-axes diffractometer equipped with a graphite diffracted beam monochrometer. The diffraction patterns were obtained by two modes of measurements. One was the θ–2θ scan by setting the scattering vector perpendicular to the film plane to investigate the stacking of atomic planes along the film normal. The other was the rocking curve measurement to investigate the crystalline quality of films.

RESULTS AND DISCUSSION

The artificial superstructure established in the ASL was examined by XRD measurements with the scattering vector normal to the film plane. The obtained XRD patterns were composed of strong and sharp basic reflections which could be indexed as the (00L) reflections of the SnS-type structure and superlattice reflections induced by artificial periodicity. Figure 1 displays an XRD pattern of $(PbSe)_3(SnSe)_3$. The peaks observed at $2\theta=15.02°$ and 30.36° are the basic (002) and (004) reflections of the SnS-type structure, respectively. The superlattice reflections are clearly detected between them. The peak angle, full width at half maximum (FWHM) and relative integrated intensity are listed in Table I. The

Table I Observed peak position, FWHM and relative integrated intensity in $(PbSe)_3(SnSe)_3$. Calculated values of Λ and intensity are also listed.

Peak	2θ (deg.)	d (Å)	FWHM (deg.)	$I_{obs.}$	Λ	$I_{calc.}$
$(000)_{+1}$	4.85	18.22	0.20	0.298		11.3
$(002)_{-1}$	10.13	8.732	0.20	0.0555	18.16	0.0270
$(002)_0$	15.02	5.898	0.09	1.09		1.13
$(002)_{+1}$	19.93	4.455	0.24	0.0420	18.19	0.0460
$(004)_{-1}$	25.37	3.511	0.29	0.459		2.823
$(004)_0$	30.36	2.947	0.14	100	18.23	100

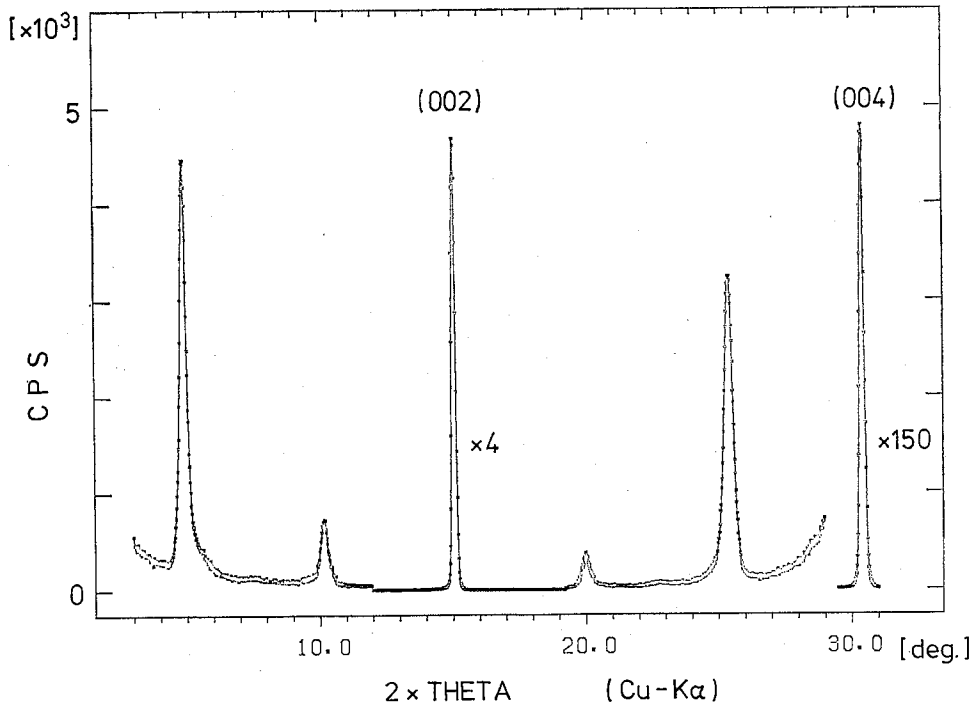

Fig. 1. XRD pattern for $(PbSe)_3(SnSe)_3$ with Λ=18.20 Å. The peaks at 2θ=15.02 and 30.36 are the basic Bragg reflections of the SnS-type structure, and the other ones are the superlattice reflections.

FWHM of the basic reflections is less than 0.15 degree (2θ), which indicates that the coherent length along the growth direction is comparable with the total film thickness. Slight broadening of the superlattice reflections was observed. The artificial period was calculated by the following formula,

$$\Lambda = \lambda/\{2(\sin\theta_0 - \sin\theta_{\pm})\},$$

where θ_0 and $\theta_{\pm}$ refer to the peak angles of the basic reflections and the $\pm$ 1st satellite reflections, respectively. The average period is 18.20 Å which is a little larger than the value of 17.68 Å expected from the commensurate structure of the tri-layer ASL: $(PbSe)_3(SnSe)_3$. The number of planes per Λ is equal to $\Lambda/d(004)_0$ and it is 6.2 for this sample. Two possible origins of this incommensurate satellite spacing have been considered. One is distribution in the number of atomic planes in each layer, m and/or n, caused by an error in thickness control. There may be, for example, some layers consisting of 4 atomic planes mixed with the majority consisting of 3 atomic planes. In that case the artificial period is locally modified to 6, 7 or, more scarcely, 8 atomic planes, giving an average of a little larger than 6 atomic planes. It is known that some ordered alloys give XRD patterns suggestive of incommensurate fractional periodicity.[5] However, electron microscopic studies revealed disordered mixing of antiphase domains having different integral periods.[6] That is, a fractional period corresponds to the average of mixed integral periods.

Similarly, the present case might correspond to a couple of periods of 6 and 7 being mixed in the ratio 4:1. Nevertheless, this can be hardly believed, considering the precision of the practically used thickness monitor with the resolution of 0.1 Å/s and the quick operation of the shutter within 0.1 s. The more probable structure will be considered below. If the amount of molecules deposited per one deposition cycle is constant but not exactly that needed to produce 3 atomic planes, incomplete planes would be stacked to produce such structure as illustrated schematically in Fig. 2 in which a sequence of $(PbSe)_{3.1}(SnSe)_{3.1}$ is assumed. An average period

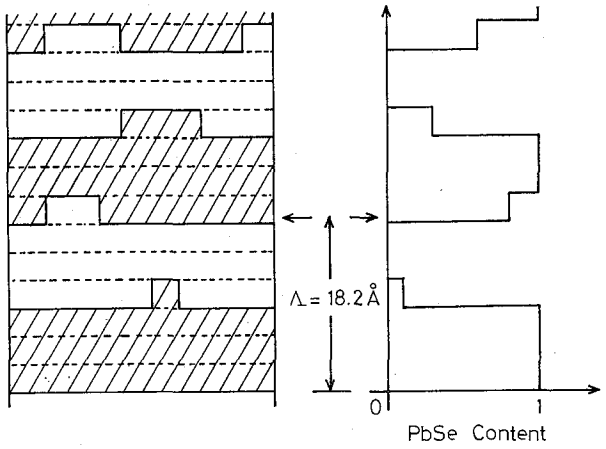

Fig. 2. Schematic structure of an incommensurate ASL. It is assumed that 3.1 atomic planes grow in one deposition cycle.

of $6.2 \cdot d(004)_0$ (=18.27 Å) and corresponding superlattice peaks can be expected from this structure. This type of "incommensurate" structure may well be assumed from the well-known tendency that both PbSe and SnSe grow along the [001] axis forming mono-atomic plane.[7] It should be pointed out that integral values of m and n do not necessarily mean the absence of mixed layers at the interface. The observed broadening of the superlattice reflections may be considered to result from the two types of incommensurate structures mentioned above.

The ideal structure of $(PbSe)_3(SnSe)_3$ is illustrated schematically in Fig. 3 (a). Since the unit cell of the SnS-type structure has four atomic planes along the c-axis, the lattice parameter of this sample should be regarded three times as large as Λ considering the compositional modulation. The SnS-type structure consists of a metal and chalcogen sublattices, each containing two different interplanar spacings. In our model of $(PbSe)_3(SnSe)_3$ in Fig. 3 (a), the following notations are assigned,

x_1 and x_2 for Pb, x_1' and x_2' for Se in the PbSe layers,

y_1 and y_2 for Sn, y_1' and y_2' for Se in the SnSe layers,

where $x_1+x_2=x_1'+x_2'$ and $y_1+y_2=y_1'+y_2'$. The average interplanar spacing of PbSe and SnSe in the ASL, $(x_1+x_2+y_1+y_2)/4$, was determined from the position

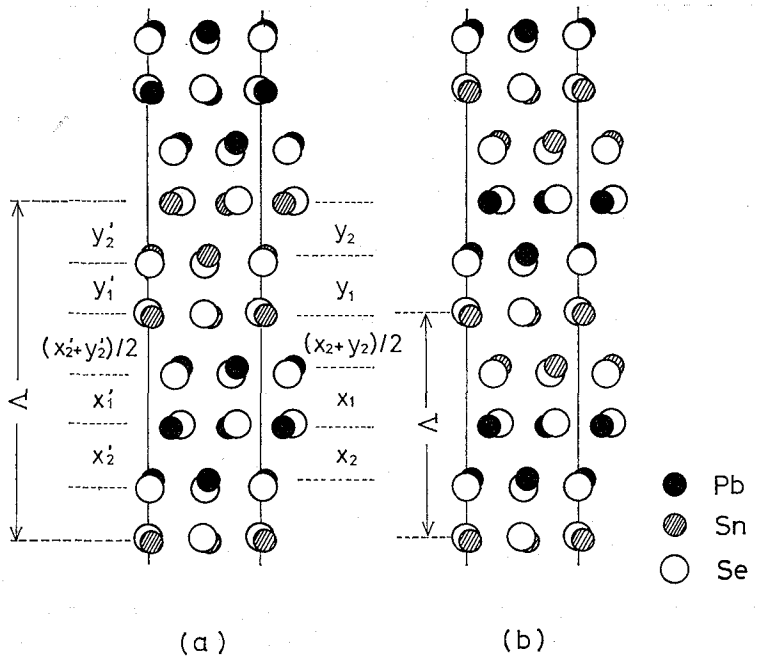

Fig. 3. Schematic models of the crystal structure for (a); $(PbSe)_3(SnSe)_3$ and (b); $(PbSe)_2(SnSe)_2$.

of the $(004)_0$ basic reflection. Then, x_1, x_2, x_1', x_2', y_1, y_2, y_1', and y_2' were estimated by considering the ratios of these values in the bulk crystal of SnSe. Using the obtained values of $x_1=3.130$ Å, $x_2=2.798$ Å, $x_1'=2.490$ Å, $x_2'=3.438$ Å, $y_1=3.065$ Å, $y_2=2.739$ Å, $y_1'=2.438$ Å, $y_2'=3.366$ Å, x-ray intensity was calculated. Comparison with the observed ones is shown in Table I. There is fairly good agreement between them, but as for the peaks of $(000)_{+1}$ and $(004)_{-1}$ some reduction was observed experimentally. It has been considered to suggest slight deviation of the ASL structure from the ideal one, like the incommensurability mentioned before.

The XRD profile of the bi-layer ASL: $(PbSe)_2(SnSe)_2$ is given in Fig. 4. Fairly strong reflections were observed at $2\theta=7.51°$ and 22.74°. The obtained data are listed in Table II. The average value of Λ is 11.72 Å and $\Lambda/d(004)=3.99$, which indicates that the film has an almost ideal commensurate structure as shown in Fig. 3 (b). Its unit cell is isomorphous with that of SnSe but half of the Sn atoms are substituted by Pb atoms. This sample should not be considered as an ordinary

Table II Observed peak position, FWHM and relative integrated intensity in $(PbSe)_2(SnSe)_2$.

Peak	2θ (deg.)	d (Å)	FWHM (deg.)	$I_{obs.}$	Λ	$I_{calc.}$
(001)	7.51	11.761	0.45	0.239		8.38
(002)	15.08	5.870	0.13	7.63	11.72	7.65
(003)	22.74	3.907	0.52	0.591	11.68	3.04
(004)	30.48	2.930	0.17	100	11.72	100

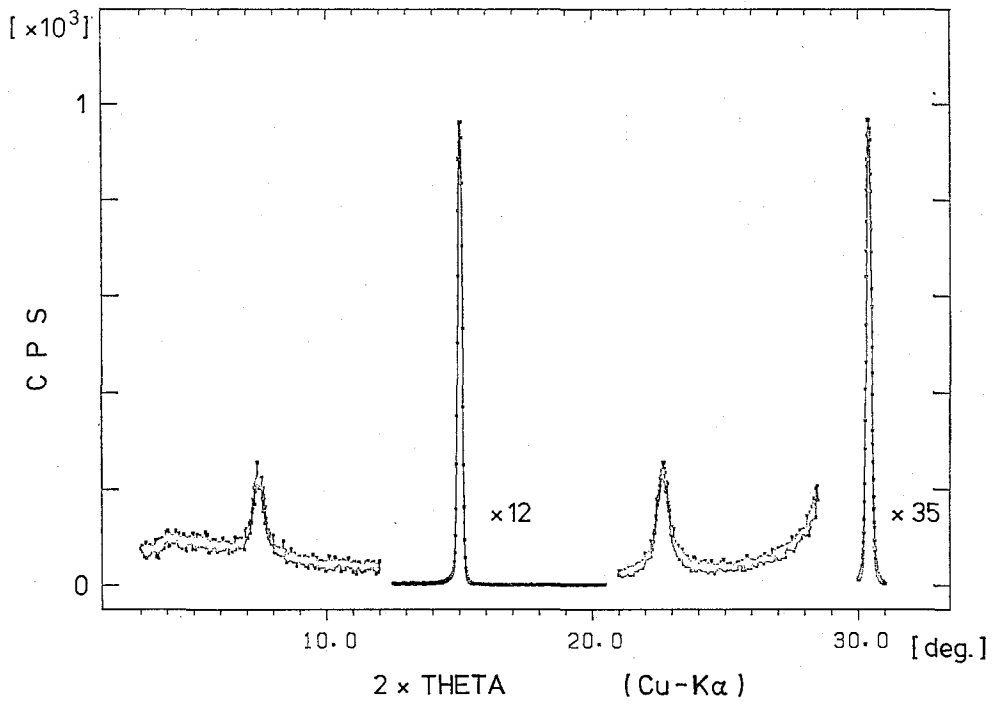

Fig. 4. XRD pattern for $(PbSe)_2(SnSe)_2$ with A=11.70 Å.

multilayered film but rather as a new compound which can not be found in nature. X-ray intensity was calculated from the model structure. The observed intensities of the (001) and (003) peaks are much smaller than the calculated ones as compared in Table II. The most probable reason for that may be that the broadening of the diffraction spots normal to the [001]* direction was ignored in the measurements of the integrated intensities. In order to decide the crystal structure of this sample in detail, three-dimensional x-ray measurements are in progress.

To examine the coherence within the film plane, rocking curves were studied around the [001] orientation. The detector (2θ-axis) was settled at the diffraction angle for the (004) lattice plane and the sample (θ-axis) was rotated. Figure 5 shows observed rocking curves for samples with (n,m)=(30,30), (8,8), (3,3) and (2,2). It was found that the peak drastically became sharp as n and m decrease. This implied that the crystalline quality was improved with decreasing sequential period. An ASL comprising thick stacked layers like $(PbSe)_{30}(SnSe)_{30}$ seems to be stabilized by introduction of misfit dislocations at the interface, which induces a distribution of the orientation of the growth plane. In contrast, the rocking curve of $(PbSe)_8(SnSe)_8$ consisting of a broad and sharp peaks suggests that the film begins to have coherent structure partly. Finally, the two lattices fit well with each other at the interface in $(PbSe)_3(SnSe)_3$ and $(PbSe)_2(SnSe)_2$ to form single crystal ASL films with almost ideal SnS-type structures shown in Fig. 3.

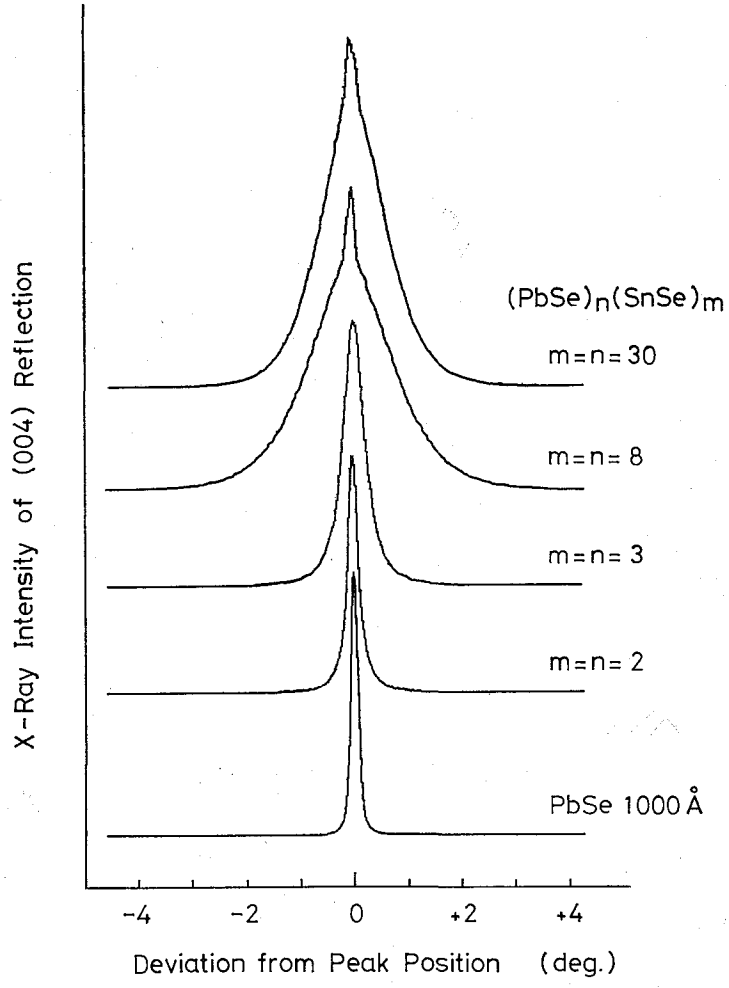

Fig. 5. The rocking curves of the (004) basic reflection for $(PbSe)_n(SnSe)_m$ with (n, m)=(30, 30), (8, 8), (3, 3) and (2, 2). That of a 1000Å-thick PbSe film is also shown for comparison.

CONCLUSIONS

We have grown $(PbSe)_n(SnSe)_m$ ASL's with (n,m)=(2,2) and (3,3) by vacuum evaporation. The XRD patterns of them were composed of strong basic reflections and well-defined superlattice reflections. The obtained values of the artificial periods showed that $(PbSe)_3(SnSe)_3$ had incommensurate structure whereas $(PbSe)_2(SnSe)_2$ did commensurate one. From the comparison of the observed x-ray intensities with the calculated ones, it was found that the films have farely good designed superstructures in spite of that they have very short periods. In addition, it was found that the crystalline quality is drastically improved by decreasing n and m, which implys that the lattices fit more coherently with thinner layer thicknesses.

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